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Cationic Polymerization of Phenylbutadienes. I. Cationic Polymerization of *trans*-1-Phenyl-1,3-butadiene

Ryuzo ASAMI,* Kan-ichi HASEGAWA, and Takuya ONOE

Department of Synthetic Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466, Japan.

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ABSTRACT: *trans*-1-Phenyl-1,3-butadiene (1-PB) was polymerized easily by Friedel—Crafts catalysts. The polymers obtained were soluble white powders. The polymer structure was determined spectroscopically; the results suggested that 1-PB was polymerized predominantly in the fashion of a 3,4-type cationic polymerization and that about a half of the 3,4-double-bonds were cyclized intramolecularly during the polymerization. In the cases of $SnCl_4$, BF_3OEt_2, and Ph_3CSnCl_5 the kinetic study was also performed. It was found in all cases that the initial rate of polymerization was proportional to the initial concentrations of both monomer and catalyst. From the molecular weight of the polymers obtained the monomer chain-transfer was shown to be mainly a terminating reaction. These kinetic results described the total scheme of cationic polymerization of this diene monomer, which was characterized by a rapid initiation. In the course of cationic polymerization of 1-PB, a colored species developed; it was followed by visible spectrum measurements. The absorption peak at 440 nm was assigned to a propagating species. The other absorption bands at 400, 493, and 570 nm were assigned to cations formed on the polymer by chain transfer.

KEY WORDS 1-Phenylbutadiene / Cationic Polymerization / Poly(1-phenylbutadiene) / Active Species / Rapid Initiation / Monomer Chain-Transfer / Cyclization /

Many problems have been solved by massive investigations of the cationic polymerization of vinyl monomers. The cationic polymerizations of cyclic conjugated dienes also have been extensively studied.[1,2] The high reactivity of cyclopentadiene has been suggested to stem from the high stabilization of the cyclopentadienyl cation.[3]

There have been relatively few investigations of the cationic polymerization of linear conjugated dienes, although many studies of dienes with anionic initiators and Ziegler—Natta catalysts have been done.[4] In the cationic polymerizations of dienes, side reactions such as cyclization and cross-linking reactions frequently offered difficulties in analyzing the kinetic data and the polymer structure.

The microstructures of diene polymers obtained in cationic polymerization have been shown in several studies. The double bonds of the polybutadienes obtained by Friedel—Crafts catalysts such as $SnCl_4$ and $AlCl_3$, were 70—80% 1,4-*trans* structure and those of polyisoprenes were about 90% 1,4-*trans*, although in both cases the content of double bonds were shown to be 20—40% and 60—80% of the monomer units, respectively.[5] The microstructures of other butadiene derivatives, 2,4-hexadiene,[6] *trans*-1-ethoxy-1,3-butadiene,[7] and 2-alkoxy-1,3-butadienes[8] were shown to be of the 1,4-type in cationic polymerizations.

In several previous works, the authors have obtained significant information regarding the reactivity and structure of phenyl-substituted butadienes from detailed studies of the anionic polymerization of these monomers.[9] Recently cationic polymerization of 1-phenylbutadiene has been reported by Masuda, *et al.*[10] In this study, the cationic polymerization of *trans*-1-phenyl-1,3-butadiene (1-PB) was performed in order to

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* A major part of this study was presented at the 19th Polymer Symposium of the Society of Polymer Science, Japan, at Kyoto, Oct., 1970. See Abstracts, p 75.

compare with the results of the anionic and the radical polymerizations of this monomer. The mechanism of cationic polymerization of 1-PB was suggested on the basis of kinetic data using triphenylmethylstannic pentachloride (Ph_3CSnCl_5), boron trifluoride etherate (BF_3OEt_2), and stannic chloride ($SnCl_4$) as catalysts. A color observed in the course of polymerization was followed spectroscopically to connect with the propagating species. The microstructure of the polymers obtained under various conditions of catalyst and solvent was also determined by means of infrared and NMR spectra.

EXPERIMENTAL

Materials

1-PB was synthesized as follows. Benzalacetone[11] formed by aldol condensation of benzaldehyde with acetone was reduced with sodium borohydride, and finally the corresponding alcohol was dehydrated with potassium bisulfate to 1-PB; bp 47—50°C (2 mm) [lit.[12] bp 83°C (11 mm)]. This monomer is all-*trans* isomer. Cinnamyl chloride was prepared according to the method of Gilman, *et al.*;[13] bp 46—50°C (0.5 mm), n_D^{18} 1.5823 [lit.[13] bp 86—87°C (2 mm), n_D^{19} 1.5820]. Gas chromatography showed they were more than 99% pure. Ph_3CSnCl_5 was synthesized from triphenylmethyl chloride (mp 110—111°C) and $SnCl_4$ in benzene using the procedure of Higashimura, *et al.*,[14] then the precipitated salt was washed with benzene twice, filtered, and diluted to the desired concentration with ethylene dichloride in ampoules with a break-seal. The concentration of the solution was determined by the absorbance at 430 nm; $\lambda_{430nm} = 1.69 \times 10^4$ l/mol cm.[14] The solvents: ethylene dichloride, benzene, cyclohexane, and toluene, and the other catalysts: $SnCl_4$, $TiCl_4$, BF_3OEt_2, $AlCl_3$, and $FeCl_3$ were purified in the usual way. The monomer, solvents, and catalysts were vigorously dried with calcium hydride or sodium metal on a high vacuum line to exclude any trace of water, and finally distilled into ampoules with a break-seal under the vacuum conditions.

Procedures

The polymerization was carried out under degassed and extremely dried condition by the break-seal technique. The rates of polymerization were followed by means of dilatometers in a water thermostat bath at 25°C. The visible spectra observed in the polymerization were measured with a quartz absorption cell under the vacuum system using a Hitachi 124 Spectrometer. After a given time, the reaction was stopped by adding methanol which contained a small amount of aqueous ammonia solution. The number-average molecular weight of poly(1-PB) was measured in benzene solution by a Hitachi 115 osmometer. The intrinsic viscosities of polymers were measured at 30°C in toluene. The IR spectrum of the polymer was measured on a KBr disk by a JASCO IR-E spectrophotometer. ^1H NMR spectrum was measured in tetrachloroethylene solution at 60 MHz on a Hitachi R-20B spectrometer.

RESULTS AND DISCUSSION

Polymerization of 1-Phenylbutadiene by Various Catalysts

As a preliminary experiment, the polymerization of 1-PB was performed by various Friedel—Crafts-type catalysts in ethylene dichloride (EDC) and in benzene. The results were shown in Table I. In all cases except iodine, soluble polymers of 1-PB were obtained in high yields. It is interesting that we found only soluble polymers in the cationic polymerization of 1-PB, while the formation of gel polymers has been reported in the cationic polymerization of butadiene and isoprene. 1-PB was shown to polymerize in hydrocarbon solvents such as benzene and toluene using these metal halide catalysts without cocatalyst. All traces of water were excluded under the high vaccum system in our experimental conditions. Although the rate of polymerization was much slower in benzene than in EDC, the high polymerizability of 1-PB in comparison with styrene, which could not be polymerized under the same conditions without cocatalyst, would be ascribed to a π-complex coordination between 1-PB and metal halides. The details of the initiation mechanism and the kinetics of the polymerization will be discussed later.

Table I. Polymerization of 1-PB by various catalysts in EDC and benzene[a]

1-PB, mol/l	Catalyst, mol/l		Solvent	Time, hr	Yield, %	$[\eta]$, dl/g
0.72	$SnCl_4$	0.012	EDC	19.5	98	0.034
0.87	BF_3OEt_2	0.015	EDC	20.5	80	0.039
0.77	$AlCl_3$	0.006	EDC	20.0	97	0.119
0.75	$FeCl_3$	0.004	EDC	29.3	76	0.033
0.85	I_2	0.014	EDC	24.2	2	—
0.62	$SnCl_4$	0.023	Benzene	19.7	97	0.082
0.69	BF_3OEt_2	0.029	Benzene	17.5	43	0.039
0.59	$FeCl_3$	0.002	Benzene	15.2	10	0.035
0.75	I_2	0.011	Benzene	18.0	0	—

[a] Temperature, 30°C.

Structure of Poly(1-phenylbutadiene) Obtained in Cationic Polymerization

As can be seen in Figure 1, a strong absorption band at 965 cm^{-1} due to the out-of-plane vibration of *trans*-olefinic proton was observed in the IR spectra of the soluble white powder of poly(1-PB) obtained by various catalysts: Ph_3CSnCl_5, $SnCl_4$, BF_3OEt_2, $FeCl_3$, and $TiCl_4$. However, none of the strong characteristic absorption bands at 990, 965, and 910 cm^{-1} of olefinic protons were observed in the IR spectrum of poly(1-PB) obtained by $AlCl_3$. These results suggest that the polymers obtained in the cationic polymerization have a 1,4-structure or a 3,4-structure or both, but no 1,2-structure. However, the contents of the 1,4-structure or the 3,4-structure could not be determined by IR spectroscopy.

UV spectra of poly(1-PB) catalyzed by cationic and anionic initiator are shown in Figure 2. Both polymers have a strong absorption peak at 255 nm and weak absorption bands, which are characteristic of styrene, in the 280—293-nm region. It can be said that the poly(1-PB) prepared by cationic catalyst has mainly a 3,4-structure from the facts that the polymer obtained in the cationic polymerization absorbs at 255 nm (ε=8000) about three times as strongly as the polymer obtained in the anionic polymerization does, and that styrene and β-methylstyrene, which were considered to be model structures of poly(phenylbutadienes), have a strong absorption band at 248 nm (ε=14000)[15] and 251 nm (ε=17000),[15] respectively. Only in the case of $AlCl_3$ shown in Table I did the soluble polymer obtained have no absorption ascribed to olefinic double-bonds in either IR or UV spectra. This suggests that the polymer would have no double-bond structure in it but only an intramolecularly cyclized structure such as the phenylcyclohexane or indene type.

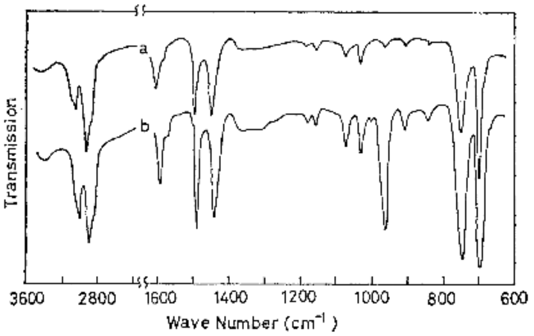


Figure 1. Infrared spectra of poly(1-PB): a, $AlCl_3$; b, $SnCl_4$.

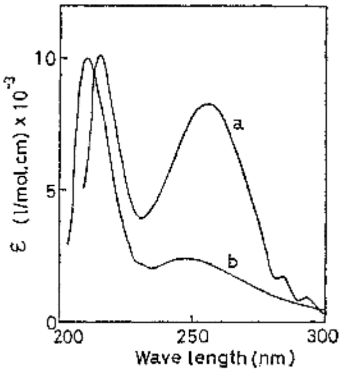
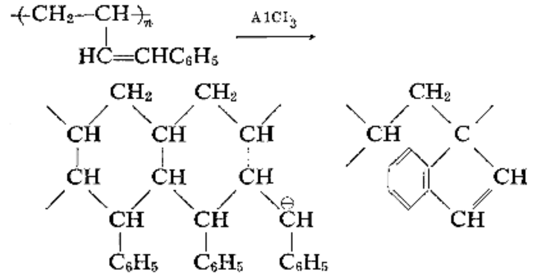


Figure 2. Ultraviolet spectra of poly(1-PB): a, cationic; b, anionic.



The isomerization of the 3, 4-structure of poly(1-PB) to cyclized structures by $AlCl_3$ would be considered reasonable, but the details were not studied.

NMR spectra of poly(1-PB) obtained in the cationic polymerization and poly(1-PB) obtained by Na—naphthalene in tetrahydrofuran (THF) are shown in Figure 3. The signals at 3.8τ and 4.7τ were assigned to a 3, 4-type and a 1, 4-type olefinic proton, respectively. The relative peak areas of the proton signals of poly(1-PB) obtained by various catalysts and the contents of the calculated microstructures are listed in Table II. An olefinic double bond of poly(1-PB) produced by an initial concentration of catalysts in the range of 10—10^{-1} mmol/*l* was shown to isomerize to a saturated bond to the extent of 30—50%, and the peak area centered at 8τ increased as the olefinic double bond decreased.

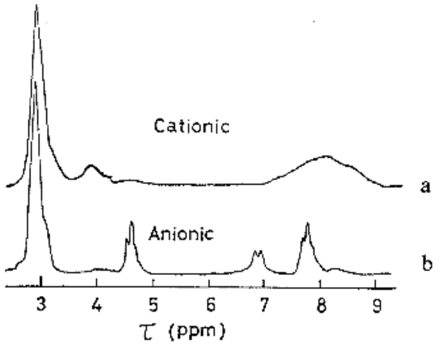


Figure 3. NMR spectra of poly(1-PB): a, poly(1-PB) obtained by $SnCl_4$ in EDC; b, poly(1-PB) obtained by Na—naphthalene in THF.

From the results of IR, UV, and NMR spectroscopy it was found that the cationic polymerization of 1-PB produced mainly 3, 4-structures and the 3, 4-type double bond in polymer came to cyclize intramolecularly in the presence of the cationic catalyst for long durations of polymerization.

As can be seen in Table II, the 3, 4-content increased with increasing the polarity of solvent and the strength of Lewis acid. This increase of the 3, 4-content can be ascribed to the increase of loose ion-pairs at the propagating ends, from the facts that the dissociation of an ion pair is promoted in a polar solvent or by a strong catalyst[2] and that the 3, 4-addition is essentially favored by a charge dispersion of the propagating end. It has already been shown that the electrophilic addition products of 1-PB were 3, 4-adducts in the cases of hydrochlorination,[16,17] bromination,[18] chlorination,[19] chlorohydrin addition,[20,21] bromohydrin addition,[21] and sulfenyl chloride addition.[22] Therefore, it is not suprising that 1-PB polymerizes in the fashion of 3, 4-type

Table II. Microstructure of poly(1-PB)

Solvent	Catalyst	NMR proton ratio				% Microstructure[b]		
		Phenyl	Olefinic H		Others[a]	3, 4	1, 4	Cyclization of 3, 4
			3, 4	1, 4				
EDC	$SnCl_4$	5.00	0.76	0.18	4.06	91	9	58
EDC	BF_3OEt_2	5.00	0.84	0.32	3.84	84	16	50
$EtNO_2$	BF_3OEt_2	5.00	0.85	0.16	3.99	92	8	50
Toluene	BF_3OEt_2	5.00	0.70	0.53	3.77	73	27	38
Benzene	$SnCl_4$	5.00	0.88	0.34	3.78	83	17	47
Benzene	$TiCl_4$	5.00	0.83	0.40	3.77	80	20	48
Cyclohexane	$SnCl_4$	5.00	0.84	0.44	3.72	78	22	36

[a] Signals in the range of τ=7.0 to 9.5.

[b] The loss of the olefinic double bonds was assumed to be based on a cyclization of the 3, 4-type.

in cationic polymerization as a characteristic behavior of the carbonium ion produced.

Kinetics of Cationic Polymerization of 1-Phenylbutadiene Using $SnCl_4$, BF_3OEt_2, and Ph_3CSnCl_5 as Catalysts

The kinetic studies of the 3, 4-polymerization of 1-PB by $SnCl_4$, BF_3OEt_2, and Ph_3CSnCl_5 were performed. The time—conversion curves of 1-PB catalyzed by $SnCl_4$, BF_3OEt_2, and Ph_3CSnCl_5 in EDC at 25°C are shown in Figures 4, 5, and 6, respectively. As it can be seen from the time—conversion curves that the rates of polymerization are almost the same in all cases of $SnCl_4$, BF_3OEt_2, and Ph_3CSnCl_5, the activities of these three catalysts can be said to be almost equal in the polymerization of 1-PB in EDC. The initial rates of polymerization calculated from the initial slopes of the first-order plots of the results shown in Figures 4 and 5 are summarized in Tables III and IV, with the intrinsic

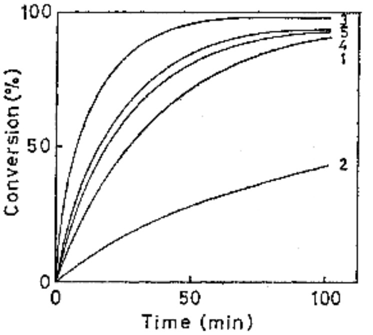


Figure 4. Time—conversion curves of polymerization of 1-PB catalyzed by $SnCl_4$ in EDC at 25°C: $[M]_0$, 0.77 *M*; $[C]_0$, 12.2 m*M* (3), 2.7 m*M* (1), 0.28 m*M* (2); $[C]_0$, 2.7—2.8 m*M*; $[M]_0$, 0.77 *M* (1), 0.39 *M* (4), 0.20 *M* (5).

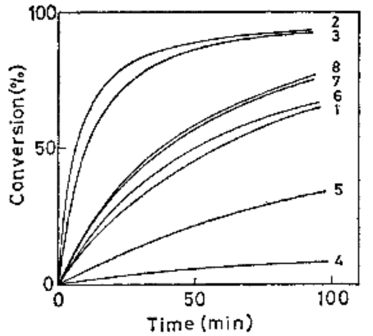


Figure 5. Time—conversion curves of polymerization of 1-PB catalyzed by BF_3OEt_2 in EDC at 25°C: $[M]_0$, 0.70 *M*; $[C]_0$, 13.2 m*M* (2), 5.9 m*M* (3), 1.8 m*M* (7), 1.6 m*M* (6), 0.46 m*M* (5), 0.15 m*M* (4); $[C]_0$, 1.8 m*M*; $[M]_0$, 1.01 *M* (1), 0.70 *M* (7), 0.33 *M* (8).

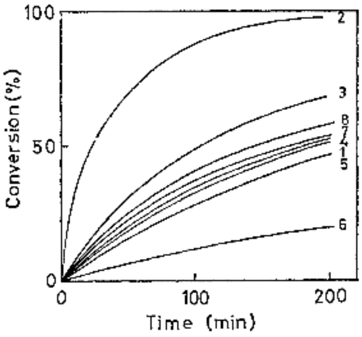


Figure 6. Time—conversion curves of polymerization of 1-PB catalyzed by Ph_3CSnCl_5 in EDC at 25°C: $[M]_0$, 0.60 *M*; $[C]_0$, 2.58 m*M* (2), 1.45 m*M* (3), 0.55 m*M* (4), 0.47 m*M* (5), 0.18 m*M* (6); $[C]_0$, 0.55 m*M*; $[M]_0$, 0.83 *M* (1), 0.60 *M* (4), 0.30 *M* (7), 0.10 *M* (8).

Table III. Initial rates of polymerization of 1-PB by $SnCl_4$ and intrinsic viscosities of the polymers[a]

Run no.	1-PB, mol/*l*	$SnCl_4$, mol/*l*	R_{p0}, mol/*l* min	[η], d*l*/g
1	0.77	2.7×10^{-3}	3.9×10^{-2}	0.039
2	0.77	0.28×10^{-3}	5.0×10^{-3}	0.036
3	0.77	12.2×10^{-3}	9.5×10^{-2}	0.041
4	0.39	2.8×10^{-3}	1.5×10^{-2}	0.037
5	0.20	2.7×10^{-3}	7.0×10^{-3}	0.039

[a] Solvent, EDC; temperature, 25°C.

Table IV. Initial rates of polymerization of 1-PB by BF_3OEt_2 and intrinsic viscosities of the polymers[a]

Run no.	1-PB, mol/*l*	BF_3OEt_2, mol/*l*	R_{p0}, mol/*l* min	[η], d*l*/g
1	1.01	1.8×10^{-3}	1.7×10^{-2}	0.034
2	0.72	13.2×10^{-3}	6.5×10^{-2}	0.034
3	0.72	5.9×10^{-3}	3.8×10^{-2}	0.034
4	0.70	0.15×10^{-3}	2.5×10^{-3}	0.031
5	0.69	0.46×10^{-3}	3.4×10^{-3}	0.033
6	0.68	1.6×10^{-3}	1.0×10^{-2}	0.033
7	0.68	1.8×10^{-3}	1.2×10^{-2}	0.032
8	0.33	1.7×10^{-3}	5.8×10^{-3}	0.032

[a] Solvent, EDC; temperature, 25°C.

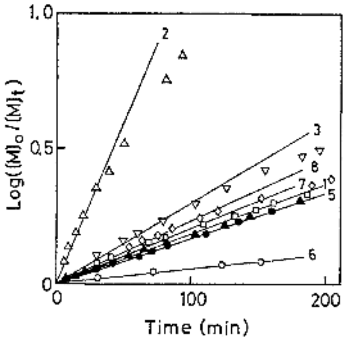


Figure 7. Polymerization of 1-PB catalyzed by Ph_3CSnCl_5. The first-order plots of Figure 6: ▲ (1); △ (2); ▽ (3); ● (5); ○ (6); □ (7); ◇ (8).

viscosities of the polymers obtained. For the case of Ph_3CSnCl_5, the first-order plots of the time—conversion curves given in Figure 6 are shown in Figure 7. A linear relation is clear between $\log [M]_0/[M]_t$ and time in the range of relatively low conversion, but at higher conversions than about 70%, the plots deviated slightly from the same line.

The rate of initiation of 1-PB by Ph_3CSnCl_5 had been followed by means of its visible spectrum and the rate was found to be expressed as follows[23]

$$\ln ([Ph_3CSnCl_5]_0/[Ph_3CSnCl_5]_t)=k[1\text{-PB}]t \quad (1)$$

In this equation, $[Ph_3CSnCl_5]_0$ and $[Ph_3CSnCl_5]_t$ represent the initial concentration and the concentration at time t of Ph_3CSnCl_5, respectively. The k was calculated to be 5.7 l/mol min. Therefore, from eq 1 it will be suggested that only 1.3 min is enough to decrease the concentration of Ph_3CSnCl_5 to 1% of the initial concentration at 0.6 mol/l of 1-PB. This means that the initiation reaction is finished much more rapidly than the propagation in cationic polymerization of 1-PB catalyzed by Ph_3CSnCl_5. The details of the initiation of phenylbutadienes will be shown in the next paper.

The relation between the initial rate of polymerization R_{p0} and the initial monomer concentration $[M]_0$ and the relation between R_{p0} and the initial concentration of catalyst $[C]_0$ are shown in Figures 8 and 9, respectively. In all cases, R_{p0} was expressed by the second-order rate of reaction which was proportional to both $[C]_0$ and $[M]_0$

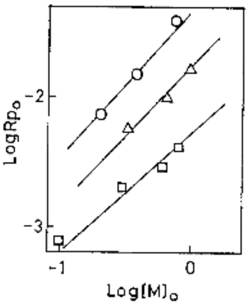


Figure 8. Dependence of $[M]_0$ on R_{p0}. Log—log plots of the initial monomer concentration and the initial rate of polymerization: ○, $SnCl_4$; △, BF_3OEt_2; □, Ph_3CSnCl_5.

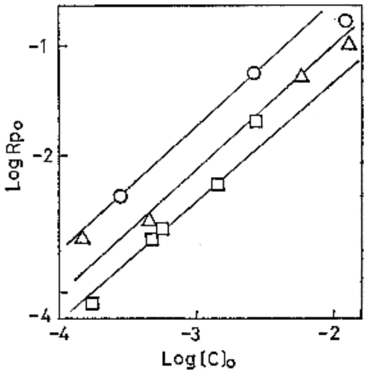


Figure 9. Dependence of $[C]_0$ on R_{p0}. Log—log plots of the catalyst concentration and the initial rate of polymerization: ○, $SnCl_4$; △, BF_3OEt_2; □, Ph_3CSnCl_5.

$$R_{p0}=k[M]_0[C]_0 \quad (2)$$

As mentioned above, it would be suggested that Ph_3CSnCl_5 was consumed within one minute for the monomer concentration used. The shapes of the time—conversion curves were also similar in the three catalysts for the corresponding conditions. Hence it is reasonable that the initiation reaction of 1-PB by $SnCl_4$ and BF_3OEt_2 proceeds as fast as by Ph_3CSnCl_5. Therefore eq 2 could be explained by a rapid initiation and a subsequent slow propagation. A similar mechanism of cationic polymerization had been offered by Pepper, *et al.*,[24] in the case of styrene catalyzed by $HClO_4$ in EDC. If we assume that all the catalysts have initiated monomers immediately, then only a slow propagation follows in the initial period of polymerization, and it is possible to calculate the bimolecular propagating constant k_p from eq 2 as follows: $k_p=0.17$ l/mol sec at 25°C for $SnCl_4$, BF_3OEt_2, and Ph_3CSnCl_5, was found. This value was shown to be close to that of $k_i=0.20$ l/mol sec, which is the bimolecular initiation rate constant of Ph_3CSnCl_5 for 1-PB. This fact clearly confirms that the initiation reaction is much faster than that of propagation because the initial concentration of catalysts used is 10^{-3}—10^{-4} mol/l. This k_p is smaller than those of the cationic polymerization of vinyl monomers.[25] The high reactivity in initiation of 1-PB could be explained in terms of the stabilization of the cinnamyl type cation produced.

A deviation from the first-order plots shown in Figure 7 suggested that a retardation reaction takes place at high conversion; hence eq 2 could no longer be applied at this stage. For this retardation, it was considered that a chain-transfer reaction to the polymer would take place at a prolonged polymerization and even after the completion of polymerization. The active species in the polymer produced by transfer reaction were thought to be so stable that the rate of polymerization would decrease. These carbonium-ion species are also responsible for the cyclization of the double bonds in the 3,4-structure of poly(1-PB) that was mentioned already. The color change which accompanied the chain-transfer reaction to the polymer was followed by its visible spectrum and will be discussed later.

The intrinsic viscosity and the number-average degree of polymerization P_n of the polymers obtained by $SnCl_4$, BF_3OEt_2, and Ph_3CSnCl_5 were measured in order to study the effect of polymerization conditions on P_n. In the cases of $SnCl_4$ and BF_3OEt_2, the intrinsic viscosities of the polymers obtained were shown to be 0.03—0.04 dl/g regardless of either the monomer concentration or the catalyst concentration. In the case of Ph_3CSnCl_5 the same result was obtained. Therefore it can be said that a monomer-transfer reaction occurs frequently as a deactivating reaction of the polymer chain in a cationic polymerization of 1-PB. For the calculation of the monomer-transfer constant the relation between the reciprocal of P_n and the value of $(\log[M]_0-\log[M]_t)/([M]_0-[M]_t)$ is shown in Figure 10. The values of the monomer-

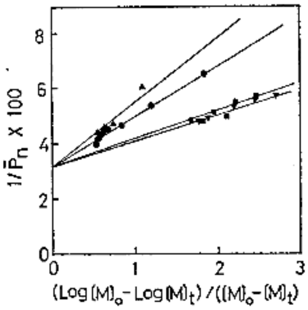


Figure 10. Effect of conversion on the degree of polymerization of polymers obtained by both $SnCl_4$ and BF_3OEt_2. $SnCl_4$: ●, $[M]_0$ 0.84 M. $[C]_0$ 0.77 mM; ■, $[M]_0$ 0.27 M, $[C]_0$ 0.80 mM. BF_3OEt_2: ▲, $[M]_0$, 0.83 M; $[C]_0$, 0.79 mM; ▼, $[M]_0$, 0.27 M; $[C]_0$, 0.80 mM.

Table V. Effect of temperature on polymerization of 1-PB

1-PB, mol/l	Catalyst, mol/l	Solvent	Temp, °C	Time, hr	Yield, %	$[\eta]$, dl/g
1.42	$SnCl_4$ 0.012	EDC	20	5	88	0.037
0.75	$SnCl_4$ 0.012	EDC	20	5	85	0.037
1.42	$SnCl_4$ 0.012	EDC	−37	5	38	0.039
0.69	$SnCl_4$ 0.012	EDC	−37	5	20	0.038
1.40	BF_3OEt_2 0.013	EDC	20	5	92	0.036
0.74	BF_3OEt_2 0.013	EDC	20	5	86	0.035
1.42	BF_3OEt_2 0.013	EDC	−35	5	41	0.045
0.72	BF_3OEt_2 0.013	EDC	−35	5	31	0.035
0.63	$SnCl_4$ 0.035	Toluene	30	20	58	0.039
0.62	$SnCl_4$ 0.035	Toluene	−78	20	76	0.044
0.61	BF_3OEt_2 0.021	Toluene	30	20	51	0.034
0.63	BF_3OEt_2 0.021	Toluene	−78	20	5	—

transfer constant $C_{tm}=k_{tm}/k_p$ calculated from the intercept of the straight line in Figure 10 are in fair agreement for both catalysts; $k_{tm}/k_p=0.32\times10^{-2}$ for $SnCl_4$ and BF_3OEt_2 at 25°C was obtained. The effect of temperature on the degree of polymerization and the polymer yields are shown in Table V. The yields were down but the intrinsic viscosities remained unchanged at low temperature.

In conclusion, the total scheme of cationic polymerization of 1-PB by $SnCl_4$, BF_3OEt_2, and Ph_3CSnCl_5 in EDC is proposed as follows

$$\text{Initiation} \qquad C^+ + M \xrightarrow{k_1} CM^+$$

$$\text{Propagation} \qquad M_n^+ + M \xrightarrow{k_p} M_{n+1}^+$$

Monomer chain transfer

$$M_n^+ + M \xrightarrow{k_{tm}} M_n + M^+$$

Polymer chain transfer

$$M_n^+ + P \xrightarrow{k_{tp}} M_n + P^+$$

where gegen anions are omitted. In the cases of $SnCl_4$ and BF_3OEt_2, the carbonium ions C^+ are shown in the following equation: $SnCl_4+RCl\rightarrow R^+SnCl_5^-$ and $BF_3OEt_2\rightarrow Et^+BF_3OEt^-$, where RCl represents the solvent EDC.

Visible Spectra in the Cationic Polymerization of 1-Phenylbutadiene

Representative spectra observed in the course of the polymerization of 1-PB catalyzed by $SnCl_4$ in EDC are shown in Figure 11. Similar spectra were observed in the case of BF_3OEt_2. An absorption band appeared in the range of 420—440 nm (absorption I) at the initial stage of polymerization and an absorption peak at 570 nm (absorption II) developed as the polymerization proceeded. In addition, two absorption bands emerged at 490 nm and at 400 nm after a prolonged polymerization. The visible spectrum of the reaction products of cinnamyl chloride with $SnCl_4$ and $AlCl_3$, as also shown in Figure 12. An absorption maximum appeared in the same region as absorption I. Therefore, it is suggested that the absorption I which appeared in the beginning is to be assigned to a cinnamyl-type cation of the propagating species. The absorption bands which emerge at 570, 490, and 400 nm as the polymerization proceeds are assigned to various cations produced by the reaction of the polymer with propagating species. In order to prove this assignment, poly(1-PB) with both cationic and anionic initiators were reacted with $SnCl_4$ in EDC. The absorption spectra obtained are shown in Figures 13 and 14. In the reaction of the cationic polymer with $SnCl_4$, absorption peaks were observed at 570, 493, and 400 nm. The features of these peaks were in accord with those of the absorption spectra at the last stage of cationic polymerization. The optical density of the absorption band at 570 nm decreased at the polymer concentration decreased. This fact implies that the band at 570 nm is clearly related to the reaction of the polymer and $SnCl_4$. The polymer recovered from this reaction showed much less content of olefinic

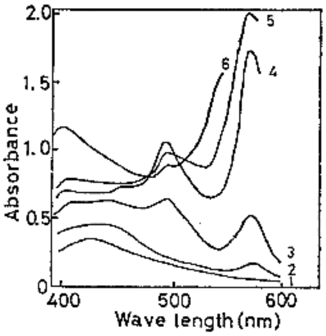


Figure 11. Visible absorption spectra observed during the polymerization of 1-PB by $SnCl_4$ in EDC at room temperature: $[M]_0$, 0.255 *M*; $[C]_0$, 29.9 m*M*; path length, 0.199 cm; polymerization time (min), 2 (1), 11 (2), 15 (3), 25 (4), 30 (5), 75 (6).

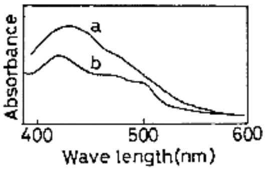


Figure 12. Visible absorption spectra observed in the reaction of cinnamyl chloride with $SnCl_4$ or $AlCl_3$ in EDC at room temperature: a ($AlCl_3$), spectrum measured immediately after mixing ($\varepsilon_{426nm}=2300$) and shifted to longer wave length ($\varepsilon_{453nm}=$ *ca.* 9000) after a long time; b ($SnCl_4$), absorption peak appeared at 420 nm immediately after mixing ($\varepsilon_{420nm}=245$). However, the absorption spectrum became complicated with increasing reaction time.

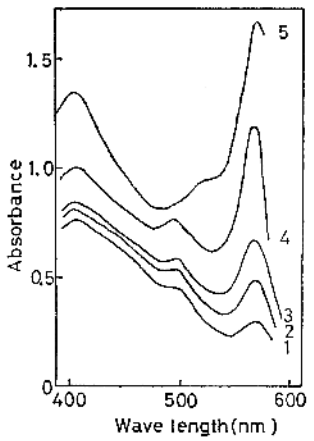


Figure 13. Absorption spectra of the reaction of poly(1-PB) obtained by $SnCl_4$ in EDC at room temperature: Concn of poly(1-PB) (monomer unit), $0.242\,M$; $[C]_0$, $29.0\,mM$; path length, 0.199 cm; reaction time (min), 1 (1), 5 (2), 12 (3), 40 (4), 120 (5).

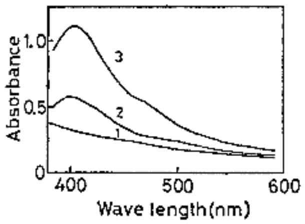


Figure 14. Absorption spectra of the reaction of poly(1-PB) obtained by Na—naphthalene in THF with $SnCl_4$ in EDC at room temperature: Concn of poly(1-PB) (monomer unit), $0.123\,M$; $[C]_0$, $58.3\,mM$; path length, 0.202 cm; reaction time, 2 min (1), 22 hr (2), 5 day (3).

double bonds than that of the original one, under IR and NMR analyses. This suggests that the cation was produced at the *trans*-olefinic double bond of the 3, 4-structure and that cyclization of the double bond took place in the reaction, whereas in the case of the polymer obtained by anionic polymerization no cyclization was observed, since this polymer was mainly of *trans*-1, 4 structure. Only the absorption peak at 400 nm appeared slowly. Therefore, the absorption band at 400 nm would be assigned to an active cation produced by hydride withdrawing from the 1, 4-type structure of the polymer.

Furthermore, the following experiment was carried out in order to make clear whether the polymer cations which appeared at the last stage of polymerization are stable in the presence of 1-PB or not. 1-PB was added to the dormant system in Figure 11. As can be seen in Figure 15, absorption II decreased slowly and, in contrast, absorption I increased. Absorption II emerged again after a prolonged polymerization. This suggests that 1-PB reacts slowly with the polymer cations.

In addition to the above experiments, the calculation by simple LCAO approximation was performed for these cation models. The transition energy of cinnamyl cation was estimated to be 1β. This value is consistent with that of benzhydryl cation (λ_{max} 441 nm)[26] or triphenylmethyl cation (λ_{max} 430 nm).[26] Cinnamyl anion was reported to absorb at 420 nm by Astaf'ev, *et al.*[27] Therefore, it is reasonable that a absorption maximum of the propagating species exists in the neighborhood of that of the benzhydryl cation and triphenylmethyl cation. The transition energies of model cations in Table VI decreased according to the following order: 1,3-dimethylcinnamyl cation > 1-methylcinnamyl cation > 1,1-dimethylcinnamyl cation > 3-methylindenyl cation. This order is in fair agreement with the experimental results. The distribution of π-electron densities of 1-methylcinnamyl cation supports the assertion that the electrophilic reaction of 1-PB is a 3, 4-addition.

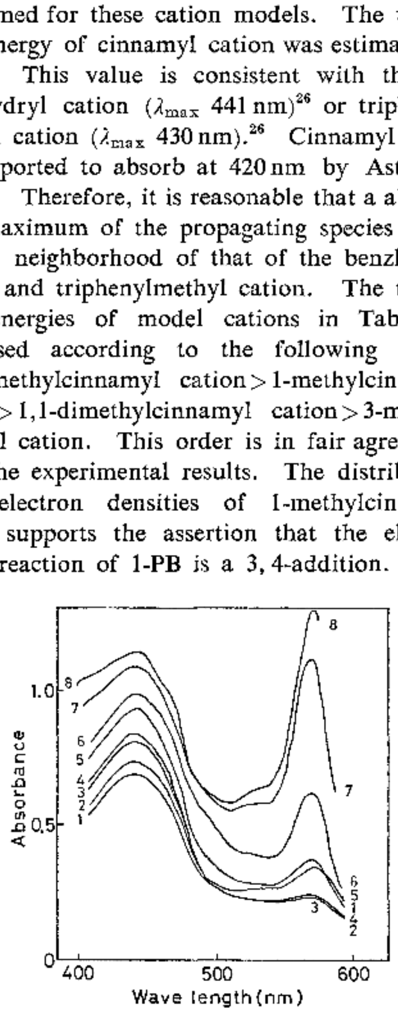
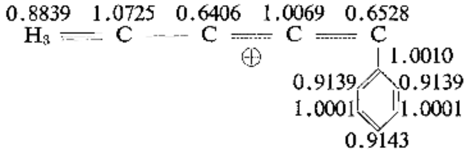


Figure 15. Effect of addition of 1-PB on the dormant polymerization system in Figure 11: Dormant polymerization time, 200 min; $[M]_0$, $0.562\,M$; $[C]_0$, $22.1\,mM$; reaction time (min), 2 (1), 8 (2), 15 (3), 20 (4), 30 (5), 40 (6), 65 (7), 80 (8).

Table VI. Transition energies[a] of model cations and π-electron densities of 1-methylcinnamyl cation by HMO approximation[b]

Cation	Transition energy, β
Cinnamyl cation	1.0000
1-Methylcinnamyl cation	0.9846
1,1-Dimethylcinnamyl cation	0.9729
1,3-Dimethylcinnamyl cation	0.9975
3-Methylindenyl cation	0.4487



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[a] The transition energy is the difference between the energy of the lowest vacant orbital and that of the highest occupied orbital.

[b] Parameter of methyl group $-\mathrm{C}\overset{0.7\beta}{\text{—}}\underset{\alpha-0.1\beta}{\mathrm{C}}\overset{2.5\beta}{\equiv}\underset{\alpha-0.5\beta}{\mathrm{H_3}}$.

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